

What is claimed is:

- 1 1. A composite electrolyte for use in electrochemical fuel cells, comprising:
  - 2 (i) an inorganic cation exchange material;
  - 3 (ii) a silica-based material; and
  - 4 (iii) a proton conducting polymer-based material, wherein the inorganic cation
  - 5 exchange material comprises about 0.1 wt% to about 99 wt% of the composite
  - 6 electrolyte.
- 1 2. The composite electrolyte of claim 1, wherein the silica-based material comprises  
2 about 0.1 wt% to about 70 wt%, and the proton conducting polymer-based material  
3 comprises about 0.1 wt% to 99.9 wt% of the composite electrolyte.
- 1 3 The composite electrolyte of claim 1 wherein the inorganic cation exchange material  
2 is selected from the group consisting of clay, zeolite, hydrous oxide, and inorganic salt.
- 1 4. The composite electrolyte of claim 3, wherein the clay includes an aluminosilicate-  
2 based exchange material selected from the group consisting of montmorillonite, kaolinite,  
3 vermiculite, smectite, hectorite, mica, bentonite, nontronite, beidellite, volkonskoite,  
4 saponite, magadite, kenyaite, zeolite, alumina, rutile.
- 1 5. The composite material of claim 3, wherein the clay is modified to make it more  
2 compatible with organic matrices, a clay modification including exfoliation which helps to  
3 separate platelets of inorganic substance.
- 1 6. The composite electrolyte of claim 3, wherein the clay includes a modified  
2 montmorillonite consisting of montmorillonite treated with a modifier material selected from  
3 a group consisting of aminododecanoic acid, trimethyl stearate ammonium, octadecylamine,  
4 and methyl dihydroxy hydrogenated tallow ammonium.
- 1 7. The composite electrolyte of claim 1 wherein the inorganic cation exchange material  
2 comprises about 0.1 wt% to about 30 wt%, the silica-based material comprises about 0.1 wt%  
3 to about 30 wt%, and the proton conducting polymer-based material comprises about 40 wt%  
4 to 99.9 wt% of the composite electrolyte.

- 1 8. The composite electrolyte of claim 1 wherein the proton conducting polymer-based  
2 material has a linear, branched, or network morphology.
- 1 9. The composite electrolyte of claim 1 wherein the proton conducting polymer-based  
2 material includes material selected from the group consisting of  
3 acrylonitrile/butadiene/styrene rubber (ABS), styrene butadiene/acrylate/acetate polymer  
4 blends, epoxides, and a thermoplastic material.
- 1 10. The composite electrolyte of claim 9 wherein the thermoplastic material is selected  
2 from a group consisting polypropylene, polycarbonate, polystyrene, polyethylene, polyaryl  
3 ethers sulfones, poly aryl ether ketone, and polysulfones.
- 1 11. The composite electrolyte of claim 1 wherein the proton conducting polymer-based  
2 material has a functional group element selected from a group consisting of sulfonate,  
3 phosphate, carbonate, amide, and imide, wherein each such functional group element has  
4 proton conducting capabilities.
- 1 12. The composite electrolyte of claim 1, further comprising an additive selected from a  
2 group consisting of preservative, thixotropy and viscosity control agent, crosslinking agent,  
3 conditioner, plasticizer, water control agent, and proton conducting material.
- 1 13. The composite electrolyte of claim 1 wherein the inorganic cation exchange material,  
2 the silica-based material and the proton conducting polymer-based material comprise 90 wt  
3 % or more of the solids content of the composite electrolyte.
- 1 14. The composite electrolyte of claim 1 wherein the composite electrolyte when  
2 measured in the substantially dried state consists essentially of the inorganic cation exchange  
3 material, the silica-based material and the proton conducting polymer-based material.
- 1 15. The composite electrolyte of claim 1 wherein the composite electrolyte has a proton  
2 conductivity of about 0.05 S/cm or higher

1 16. The composite electrolyte of claim 1 wherein the silica-based material includes  
2 materials containing one or more of silica, silicate, and silicate having an organic element.

1 17. The composite electrolyte of claim 1 wherein the silica-based material is either  
2 colloidal silica containing discrete spheres of silica or tetraethylorthosilicate.

1 18. An electrochemical fuel cell, comprising:

2 (i) an anode;

3 (ii) a cathode;

4 (iii) a fuel supply to the anode;

5 (iv) an oxidant supply to the cathode; and

6 (v) a composite electrolyte positioned between the anode and cathode and  
7 including

8 (a) an inorganic cation material,

9 (b) a silica-based binder, and

10 (c) a polymer-based binder,

11 wherein the inorganic cation exchange material comprises about 0.1 wt% to about 99  
12 wt%, of the composite electrolyte.

1 19. The electrochemical fuel cell of claim 18 wherein the silica-based material comprises  
2 about 0.1 wt% to about 70 wt%, and the proton conducting polymer-based material  
3 comprises about 0.1 wt% to 99.9 wt% of the composite electrolyte.

1 20. The electrochemical fuel cell of claim 18 wherein the inorganic cation exchange  
2 material comprises about 0.1 wt% to about 30 wt%, the silica-based material comprises about  
3 0.1 wt% to about 30 wt%, and the proton conducting polymer-based material comprises  
4 about 40 wt% to 99.9 wt% of the composite electrolyte.

1 21. The electrochemical fuel cell of claim 18 wherein the inorganic cation exchange  
2 material is selected from the group consisting of clay, zeolite, hydrous oxide, and inorganic  
3 salt.

1 22. The electrochemical fuel cell of claim 21 wherein the clay includes an  
2 aluminosilicate-based exchange material selected from the group consisting of

3 montmorillonite, kaolinite, vermiculite, smectite, hectorite, mica, bentonite, nontronite,  
4 beidellite, volkonskoite, saponite, magadite, kenyaite, zeolite, alumina, and rutile.

1 23. The electrochemical fuel cell of claim 21, wherein the clay is modified to make it  
2 more compatible with organic matrices, a clay modification including exfoliation which helps  
3 to separate platelets of inorganic substance.

1 24. The electrochemical fuel cell of claim 21, wherein the clay includes a modified  
2 montmorillonite consisting of montmorillonite treated with a modifier material selected from  
3 a group consisting of aminododecanoic acid, trimethyl stearate ammonium, octadecylamine,  
4 and methyl dihydroxy hydrogenated tallow ammonium.

1 25. The electrochemical fuel cell of claim 18 wherein the polymer-based material has  
2 linear, branched, or network morphology.

1 26. The electrochemical fuel cell of claim 18 wherein the polymer-based material  
2 includes material selected from the group consisting of acrylonitrile/butadiene/styrene rubber  
3 (ABS), styrene butadiene/acrylate/acetate polymer blends, epoxides, polypropylene,  
4 polycarbonate, polystyrene, polyethylene, polyaryl ethers, and polysulfones.

1 27. The electrochemical fuel cell of claim 18 wherein the inorganic cation exchange  
2 material, the silica-based material and the polymer-based material comprise 90 wt % or more  
3 of the solids content of the composite electrolyte.

1 28. The electrochemical fuel cell of claim 18 wherein the composite electrolyte when  
2 measured in the substantially dried state consists essentially of the inorganic cation exchange  
3 material, the silica-based material and the polymer-based material.

1 29. The electrochemical fuel cell of claim 18 wherein the composite electrolyte has a  
2 proton conductivity of about 0.05 S/cm or higher.

1 30. A method of fabricating a composite electrolyte for use in an electrochemical fuel  
2 cell, comprising:

3 (i) applying onto a surface of a substrate a viscous liquid composition of (a) an  
4 inorganic cation exchange material, (b) silica-based material, (c) a polymer-  
5 based material, and (d) a solvent-dispersant;  
6 (ii) spreading the viscous liquid composition to form a uniform thickness layer on  
7 the substrate; and  
8 (iii) allowing the solvent to evaporate from the viscous liquid composition to yield  
9 the composite electrolyte,  
10 wherein the inorganic cation exchange material comprises about 0.1 wt% to  
11 about 99 wt% of the composite electrolyte.

1 31. The method of claim 30, wherein the silica-based material comprises about 0.1 wt%  
2 to about 70 wt%, and the polymer-based material comprises about 0.1 wt% to 99.9 wt% of  
3 the composite electrolyte.

1 32. The method of claim 30 wherein step (ii) includes drawing the viscous liquid  
2 composition through a doctor blade assembly.

1 33. The method of claim 30 wherein step (iii) includes heating the viscous liquid  
2 composition.

1 34. The method of claim 30 wherein the inorganic cation exchange material comprises  
2 about 0.1 wt% to about 30 wt%, the silica-based material comprises about 0.1 wt% to about  
3 15 wt%, and the polymer-based material comprises about 40 wt% to 99 wt% of the composite  
4 electrolyte.

1 35. The method of claim 19 wherein the inorganic cation exchange material is selected  
2 from the group consisting of clay, zeolite, hydrous oxide, inorganic and salt.

1 36. The method of claim 35 wherein the clay includes an aluminosilicate-based exchange  
2 material selected from the group consisting of montmorillonite, kaolinite, vermiculite,  
3 smectite, hectorite, mica, bentonite, nontronite, beidellite, volkonskoite, saponite, magadite,  
4 kenyaite, zeolite, alumina, and rutile.

- 1 37. The method of claim 35, wherein the clay is modified to make it more compatible  
2 with organic matrices, a clay modification including exfoliation which helps to separate  
3 platelets of inorganic substance.
- 1 38. The method of claim 35, wherein the clay includes a modified montmorillonite  
2 consisting of montmorillonite treated with a modifier material selected from a group  
3 consisting of aminododecanoic acid, trimethyl stearate ammonium, octadecylamine, and  
4 methyl dihydroxy hydrogenated tallow ammonium.
- 1 39. The method of claim 30 wherein the polymer-based material has a linear, branched, or  
2 netted morphology.
- 1 40. The method of claim 30 wherein the polymer-based material includes one of  
2 acrylonitrile/butadiene/styrene rubber (ABS), styrene butadiene/acrylate/acetate polymer  
3 blends, epoxides, polypropylene, polycarbonate, polystyrene, polyethylene, polyaryl ethers,  
4 and polysulfones.
- 1 41. The method of claim 30 wherein the solvent-dispersant comprises water, N-methyl  
2 pyrrolidinone, dimethyl sulfoxide, dimethyl acidimide, and dimethylformamide.
- 1 42. The method of claim 30 wherein the inorganic cation exchange material, the silica-  
2 based material and the polymer-based material comprise 90 wt % or more of the solids  
3 content of the composite electrolyte.
- 1 43. The method of claim 30 wherein the composite electrolyte when measured in the  
2 substantially dried state consists essentially of the inorganic cation exchange material, the  
3 silica-based material and the polymer-based material.
- 1 44. The method of claim 19 wherein the composite electrolyte has a proton conductivity  
2 of about 0.05 S/cm or higher.
- 1 45. A method for producing a composite membrane, comprising:

- 2 (i) grinding a sulfonated polyether ether ketone (SPEEK) and clay mixture and
- 3 dissolving the mixture in a distilled dimethylformamide (DMF) to form a solution;
- 4 (ii) heating the solution until it thickens and attains a casting consistency;
- 5 (iii) degassing the solution in a vacuum oven;
- 6 (iv) casting the solution into a film on a glass surface using a doctor blade;
- 7 (v) curing the film; and
- 8 (vi) peeling the film from the glass.

1 46. The method of claim 45, wherein the dissolving in step (i) is performed by stirring  
2 for about 2 hours using a magnetic stir bar.

1 47. The method of claim 45, wherein the solution is stirred while heated, and wherein the  
2 DMF evaporates.

1 48. The method of claim 45, wherein the film is about 60  $\mu\text{m}$  thick.

1 49. The method of claim 45, wherein the curing includes,  
2 (a) annealing the film in a convection oven, and  
3 (b) maintaining the film in a vacuum for a predetermined time period at a  
4 predetermined temperature.

1 50. The method of claim 45, further comprising:  
2 storing the film in ultra-pure water until it is ready for use.